

# Current Streamline Flow on Current-induced Effects in Highly Asymmetric Molecular Junctions.

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From first-principles approaches, we illustrate that the current-induced forces and the selection rule for inelastic effects are highly relevant to the current density in an asymmetric molecular junction. The curved flow of current streamline around the asymmetric molecule may induce a net torque, which tends to rotate the benzene molecule, similar to the way a stream of water rotates a waterwheel. Thus, the Pt/benzene junction offers a practical system in the exploration of the possibility of atomic-scale motors. We also enumerate examples to show that the use of selection rule can lead to misjudgement of the importance of normal modes in the inelastic profiles when the detailed information about the current density is not considered.

Electron transport in a single-molecule molecular junction, where the molecule is sandwiched between two electrodes, has been investigated extensively in the pursuit of extreme device miniaturization [1–4]. A major concern for single-molecule junctions is the fundamental properties of current-induced effects due to nonequilibrium electron transport at finite biases. These effects are efficient tools to explore the single-molecule signatures from quantum mechanical perspectives, and thus are important and interesting from theoretical and experimental points of view. For example, the question on whether the current-induced forces on atoms are conserved has been raised [5]. Through molecular dynamics simulations, it has been recently reported that the current-induced forces are generally not conserved [6, 7]. The authors show that it is possible to construct atomic-scale systems where the current-induced forces can be used to rotate the atoms. Therefore, the current-induced forces are not conserved due to the nonzero net work done by the current-induced forces [7].

The current-induced effects with nuclear degrees of freedom of molecules can enrich the understanding of the interactions between electrons and molecular vibrations. In the hydrogen junctions, the mode identification and the selection rule for modes that significantly contribute to IETS are related to the large component of vibration along the direction of electron transport ( $z$ -direction) [8]. Due to the short length of the junction, electrons are transported quasi-ballistically in the molecular junction [9]. Consequently, both the interaction between electrons and local ions (electron-vibration interaction) and the induced local heating need to be considered. [10–13]. Electron-vibration interaction reveals the junction signatures through the inelastic electron tunneling spectroscopy (IETS) [14, 15], while local temperature resulting from local heating can be obtained by equilibrating the heat generation in the junction with heat dissipation to the electrodes. Recent report shows that local heating leads to a stronger suppression of the current at longitudinal vibrational modes for a 4-Al atomic wire [16].

Moreover, Kiguchi *et al.* have measured a high con-

ductance in a single-molecule junction where the benzene molecule is connected directly to the platinum electrodes (Pt/benzene junction) [17]. This demonstrates the feasibility of a carbon-metal link. The authors have concluded that the benzene molecule forms a direct bond with the electrodes. This is based on the analysis of the conductance histogram and IETS, where the vibrational modes in the inelastic profiles have been verified by isotope substitution. The relaxed configuration of the Pt/benzene junction, as we shall show later, loses mirror symmetry. The highly tilted benzene molecule causes the streamline flow of the current to curve considerably to one side of the benzene ring. This could cause the unbalanced current-induced forces, which tend to rotate the benzene molecule. Moreover, the mode selection rule for IETS in the highly tilted benzene molecule junction becomes intricate. The selection rule based on the component of vibrations along the  $z$ -direction turns out to be inappropriate. Determining the importance the contribution of normal modes to IETS based only on the  $z$ -component of vibrations will lead to misjudgement. This suggests the necessity of looking into the detailed current density, especially in highly asymmetric molecular junctions, such as the Pt/benzene junction.

In this Letter, we demonstrate that the current-induced effects are highly relevant to the details of the current density. This is particularly important in the Pt/benzene junction because of its highly asymmetric configuration. From first-principles approaches, we investigate the impact of asymmetric current streamline flow on the current-induced forces and the selection rule for IETS in the Pt/benzene junction. It should be noted that our theoretical method has an advantage over the DFT+nonequilibrium Green function method since the latter does not offer information about *current density*. We show that the curved current streamline flow around the molecule may induce a net torque, which tends to rotate the benzene molecule. To compare with the experimental IETS data, we calculate the inelastic profile of conductance ( $dI/dV$ ) and the derivative of conductance ( $d^2I/dV^2$ ) with and without local heating. Counterexamples are provided to show that the selection rule

for important normal modes based on the component of vibrations along the  $z$ -direction is inadequate.

We start with a brief introduction to the theories which lead to the results of our calculations. We study the current-induced forces and inelastic profiles in the framework of density functional theory (DFT) in scattering approaches [18]. The wavefunctions  $\Psi_{EK_{\parallel}}^{\alpha}(\mathbf{r})$  are calculated by solving the Lippmann-Schwinger equation iteratively until self-consistency is obtained.

The force  $\mathbf{F}$ , acting on a given atom at position  $\mathbf{R}$  exerted by the nonequilibrium current, is given by the Hellmann-Feynman type of theorem which has been developed in Ref. [19].

$$\mathbf{F} = \sum_i \langle \psi_i | \frac{\partial \mathbf{H}}{\partial \mathbf{R}} | \psi_i \rangle + \lim_{\Delta \rightarrow 0} \int_{\sigma} d\mathbf{E} \langle \psi_{\Delta} | \frac{\partial \mathbf{H}}{\partial \mathbf{R}} | \psi_{\Delta} \rangle, \quad (1)$$

where the first term on the right hand side of Eq. 1 is the Hellmann-Feynman contribution to the force due to localized electronic states  $|\psi_i\rangle$ . The second term is the contribution to the force from the continuum states  $|\psi_{\Delta}\rangle$ .

The inelastic current and local heating are calculated using the first-order perturbation theory based on the second-quantized formalism. By applying the field operator with the wavefunctions obtained in DFT, the many-body Hamiltonian of the system is  $H = H_{el} + H_{vib} + H_{el-vib}$ , where  $H_{el}$  is the electronic part under adiabatic approximations;  $H_{vib}$  is the ionic part of the Hamiltonian, which can be casted into a set of independent simple harmonic oscillators via normal coordinates; and  $H_{el-vib}$  represents the electron-vibration interactions and has the form

$$H_{el-vib} = \sum_{\alpha, \beta, E_1, E_2, j} \left( \sum_{i, \mu} \sqrt{\frac{\hbar}{2M_i\omega_j}} A_{i\mu, j} J_{E_1, E_2}^{i\mu, \alpha\beta} \right) \times a_{E_1}^{\alpha\dagger} a_{E_2}^{\beta} (b_j + b_j^{\dagger}), \quad (2)$$

where  $\alpha$  and  $\beta$  refers to either the left (L) or the right (R) electrodes;  $M_i$  is the mass of the  $i$ -th atom;  $A_{i\mu, j}$  is a canonical transformation between normal and cartesian coordinates satisfying  $\sum_{i, \mu} A_{i\mu, j} A_{i\mu, j'} = \delta_{j, j'}$ ;  $\omega_j$  are the normal mode frequencies;  $b_j$  is the annihilation operator for phonons corresponding to the  $j$ -th normal mode; and  $a^{L(R)}$  is the annihilation operator for electrons. The coupling constant  $J_{E_1, E_2}^{i\mu, \alpha\beta}$  between electrons and the vibration of the  $i$ -th atom in  $\mu$ -th ( $\mu = x, y, z$ ) component, i.e.,

$$J_{E_1, E_2}^{i\mu, \alpha\beta} = \int d\mathbf{r} \int d\mathbf{K}_{\parallel} [\Psi_{E_1 \mathbf{K}_{\parallel}}^{\alpha}(\mathbf{r})]^* [\partial_{\mu} V^{ps}(\mathbf{r}, \mathbf{R}_i) \Psi_{E_2 \mathbf{K}_{\parallel}}^{\beta}(\mathbf{r})], \quad (3)$$

where  $V^{ps}(\mathbf{r}, \mathbf{R}_i)$  is the pseudopotential representing the interaction between the electron at  $\mathbf{r}$  and the  $i$ -th ion at  $\mathbf{R}_i$ .

The current in the presence of electron-vibration scattering within the first-order correction is, [16],

$$I = \frac{2e}{h} \int dE [(f_E^R - f_E^L) - (\tilde{B}^R - \tilde{B}^L)] \tau(E), \quad (4)$$

where  $f_E^{L(R)} = 1/[\exp((E - \mu_{L(R)})/(k_B T_{L(R)})) + 1]$  is the Fermi-Dirac distribution function for the left(right) electrode,  $k_B$  is the Boltzmann constant,  $\mu_{L(R)}$  the chemical potential in left(right) electrode,  $T_{L(R)}$  is the temperature in the left(right) electrode, and  $\tau(E) = \frac{\pi \hbar^2}{mi} \int d\mathbf{R} \int d\mathbf{K}_{\parallel} (\Psi_E^{R*} \nabla \Psi_E^R - \nabla \Psi_E^{R*} \Psi_E^R)$  is the transmission function of electrons with the energy  $E$  from the right electrode. In the absence of electron-vibration interactions, Eq. (4) returns to the Landauer-Büttiker current formula. The normalized parameters  $\tilde{B}^{\alpha}$  ( $\alpha = L, R$ ) from the inelastic scattering processes are obtained by the following equations:

$$\tilde{B}^{\alpha} = \sum_{j\nu} [(|B_{j\nu, k}^{\beta\alpha}|^2) f_E^{\alpha} (1 - f_{E \pm \hbar\omega_{j\nu}}^{\beta})], \quad (5)$$

where  $\{\alpha, \beta\} = \{L, R\}$  and  $\alpha \neq \beta$ . The parameter  $B_{j\nu, 1(2)}^{\beta\alpha}$  in Eq. (5) is,

$$B_{j\nu, 1(2)}^{\beta\alpha} = i\pi \sum_{i\mu} \sqrt{\frac{\hbar}{2\omega_{j\nu}}} A_{i\mu, j\nu} J_{E \pm \hbar\omega_{j\nu}, E}^{i\mu, \beta\alpha} D_{E \pm \hbar\omega_{j\nu}}^{\beta} \times \sqrt{\delta + n_{j\nu}}, \quad (6)$$

where  $\delta = 0(1)$  represents the process of phonon absorption(emission), and  $n_{j\nu} = 1/[\exp(\hbar\omega_{j\nu}/k_B T_w) - 1]$  denotes the ensemble averages of phonon states where  $T_w$  is the local temperature.  $\langle B_{j\nu, k}^{\beta\alpha} \rangle$  refers to the ensemble average over phonon states.

To incorporate local heating in our calculations, we compute the total thermal power generated in the junction  $P$  via electron-vibration interactions using [16],

$$P = \sum_{j \in vib} \sum_{\alpha, \beta = \{L, R\}} (W_j^{\alpha\beta, 2} - W_j^{\alpha\beta, 1}), \quad (7)$$

where  $W_j^{\alpha\beta, 2(1)}$  is the power calculated up to the first order from the Fermi golden rule, corresponding to relaxation (excitation) of the vibrational modes [10].

We consider successively the effects of the curved flow of current streamline on the current-induced forces and inelastic profiles in a highly asymmetric single-molecule junction. First, we compare the current density at 0.1 V with the forces on each atom in the Pt/benzene junction, where the current-induced forces are calculated by subtracting the total forces at 0.1 V and 0 V, as shown in Fig. 1(a). We observe that the benzene is subjected to compressional forces in both the horizontal and vertical directions. This feature is consistent with the current-induced forces for the conventional Au/benzene junction, where the benzene molecule lies on the same plane with both electrodes and exhibits mirror symmetry [20].

In the Pt/benzene junction, the horizontal compressional force on the two outermost platinum atoms is significantly stronger than the vertical force because the current flows mostly through these two atoms. Due to the tilted benzene ring with respect to the  $y - z$  plane, the net force is considerably stronger in the negative  $y$

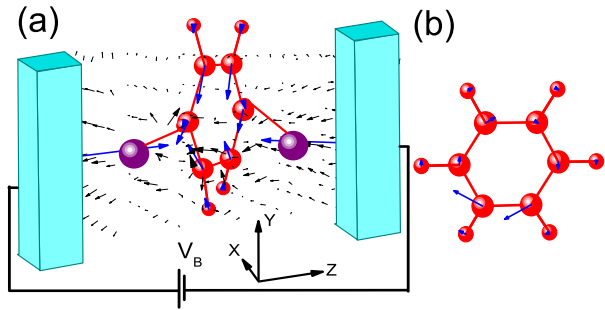


FIG. 1: (Color online). (a) 3D force vector plot (blue line) of the benzene molecule (red) connected to platinum atoms (purple) with  $V_B = 0.1$  V on top of the current density vector plot (black line). The magnitude of the current density varies in orders of magnitude. The graph is plotted in log scale to help the visualization of the smaller current density. The separation of Pt-electrodes (jellium modeled,  $r_s \approx 3$ ) is fixed at 9.626 a.u. (b) Projection of the force vectors on the plane of the benzene molecule. The projected net torque around the center of benzene ring is  $(0.0013, -1.637 \times 10^{-7}, -0.0016)$  nN-Å.

and negative  $z$  directions. The curved current streamline flow around the molecule produces a net torque around the center of the benzene ring. The net torque [around  $(0.010, -0.077, 0.005)$  nN-Å] is stronger in the negative  $y$ -direction. This means that the force induced by the curved current stream line flow could lead to a clockwise rotation in the  $x - z$  plane. We also project the force vectors onto the plane of the benzene ring, as shown in Fig. 1(b). We observe that the benzene ring experiences a net torque which tends to rotate the molecule clockwise. Thus, the highly asymmetric single-molecule junction, such as the Pt/benzene junction, offers a practical system in the exploration of the possibility that current could be used to drive atomic-scale motors.

Second, we show that the current streamline flow is crucial to explain the selection rule for normal modes shown in the IETS. Without looking into the details of current density, the selection only based on the current could lead to misjudgement with regard to the importance of normal modes for IETS in the Pt/benzene junction and other highly asymmetric molecular junctions.

In Fig. 2(a), four modes denoted as (I), (II), (III) and (IV) out of 42 vibrational modes with normal mode energies around 42 eV, 64 eV, 80 eV, and 93 eV, respectively, are shown. Mode (I) is acoustic-like and contributes to IETS at  $V_B = 42$  mV, which has been experimentally observed [17]. This mode corresponds to a vibration of the benzene molecule as a whole, with a large component of motion along the current. In other words, the center of mass of the benzene molecule moves along the  $z$ -direction. Mode (II) is a longitudinal mode where the middle part vibrates in the direction opposite to those of the top and the bottom parts. Mode (III) is a transverse mode where the left side of the carbon ring vibrates downwards while the right-side vibrates upwards. This

mode has also been observed in the IETS but has not been discussed in Ref. [17]. Mode (IV) is another longitudinal mode. However, only the second-nearest neighbor vibrates in the same direction. The center of mass of the benzene molecule remains fixed.

To include the effects of local heating, we obtain the rate of thermal energy dissipated to the bulk electrodes via phonon-phonon interactions using the weak-link model [21]. The stiffness of the benzene molecule is estimated using the total energy calculation, which gives  $K = 6.67302 \times 10^{-4} \text{ eV}_0/a_0^2$ , where  $a_0$  is the Bohr radius. The effective local temperature  $T_w$  is achieved when heat generation in the nanostructure and heat dissipation into the bulk electrodes are balanced [10]. Fig. 2(b) shows the effective local temperature  $T_w$  vs.  $V_B$  in a Pt/benzene junction, where the temperatures of bulk Pt electrodes are set to 0 K. We observe that the local temperature increases rapidly when the bias is larger than  $V_B = 42$  mV, where the electrons have enough energy to excite mode (I), the lowest energy mode vibrating along the  $z$ -direction.

Subsequently, we calculate the inelastic profile of conductance ( $dI/dV$ ) [upper panel in Fig. 2(c)] and the absolute value of the differential conductance ( $d^2I/dV^2$ ) [lower panel in Fig. 2(c)], with and without the presence of local heating, as a function of bias voltage. The zero-bias conductance (approximately  $0.58 G_0$ ) is in agreement with the large conductance observed in the experiments [17]. This is in sharp contrast to the small conductance which has been found in the conventional junction, where the benzene molecule is connected to the gold electrodes via the sulfur atoms. When local heating is included, we observe that the inelastic features are enhanced due to increased number of local

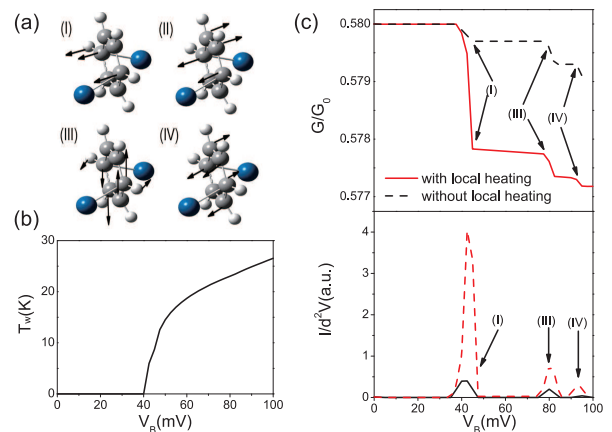


FIG. 2: (Color online). (a) Four vibrational modes corresponding to energies (I) 42 eV, (II) 64 eV, (III) 80 eV, and (IV) 93 eV. (b) Local temperature  $T_w$  as a function of the applied bias  $V_B$  at zero electrode temperature. (c) Conductance and the derivative of conductance as a function of the applied bias  $V_B$  with local heating (red and dashed) and without local heating (black and solid). Temperatures of electrodes are set to zero.

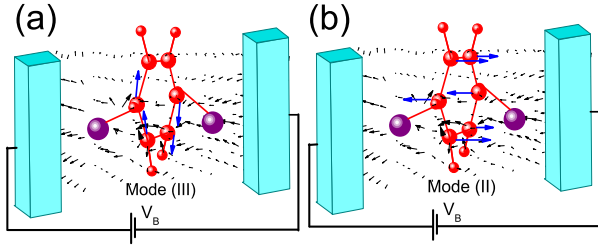


FIG. 3: (Color online). (a) Schematic of Mode (III) and (b) Mode (II) with vibrational direction (blue line) on top of the current density vector plot (black line) of the benzene molecule (red) connected to the platinum atoms (purple) sandwiched between two Pt electrodes with a bias voltage of  $V_B = 0.1$  V.

phonons. Figure 2(c) shows that large jumps in IETS correspond to three normal modes [Modes (I), (III), and (IV)]. Modes (I) and (IV) clearly show a large component of vibration along the direction of electron transport (i.e., roughly along the line connecting two Pt atoms), as shown in Fig. 2(a). The large contributions of these two modes can be explained by the selection rule based on the current: the strength of inelastic effects are related to the component of vibration along the  $z$ -direction [8]. However, Mode (III) is an exception to the selection rule based on the current. Fig. 2(a) indicates that Mode (III) is a transverse mode. The motion is mostly perpendicular to the line connecting the two Pt atoms, and thus, its contribution to the inelastic effects is expected to be minimal. The large contribution of Mode (III) to the IETS has posed a perplexing problem regarding the applicability of the selection rule based on the current.

To settle this problem, we visualize the current density and compare the electron current streamline flow with the motion of normal modes. It should be noted that the center of the mass (CM) of the benzene molecule does not lie in the line connecting the two platinum atoms. Under such highly asymmetric configuration, the current tends to flow through the bottom half of the benzene molecule, as shown in Fig. 3. For Mode (III), the carbon ring near the left electrode vibrates upward while the carbon-ring near the right electrode vibrates downward. Fig. 3(a) clearly shows that the carbon-ring vibrates along the curved electron current streamline flow. This justifies the importance of Mode (III) to the IETS. We illustrate another example which shows the importance of the current density on the selection rule for inelastic effects. Figure 2(c) displays that Mode (II) has a large component of motion along the  $z$ -direction, but the corresponding inelastic profile does not occur, as shown in Fig. 2(c). Figure 3(b) shows that the motion of Mode (II) is mostly transverse to the curved current streamline flow. Thus, this mode is unimportant to the IETS.

In conclusion, we have shown that the current-induced forces and inelastic profiles are highly relevant to the details of current density, especially in highly asymmetric molecular junctions. The asymmetric current streamline

flows may cause net torque, which tends to rotate the molecule, in a manner similar to a stream of water rotates a waterwheel. Thus, the highly asymmetric single-molecule junctions offer practical systems to explore the possibility of an atomic-scale motor driven by the non-equilibrium electron transport. Current density is also important in the explanation of the mode selection rule for inelastic effects. In the absence of detailed information on the current density, we enumerate examples to show that the importance of normal modes on the inelastic effects could be misjudged.

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<sup>1</sup> N. J. Tao, *Nature Nanotechnology* **1**, 173 (2006).

<sup>2</sup> A. Nitzan and M. A. Ratner, *Science* **300**, 1384 (2003).

<sup>3</sup> P. Reddy, S. Y. Jang, R. A. Segalman, and A. Majumdar, *Science* **315**, 1568 (2007).

<sup>4</sup> Y. Dubi and M. Di Ventra, *Rev. Mod. Phys.* **83**, 131 (2011).

<sup>5</sup> M. Di Ventra, Y. C. Chen, and T. N. Todorov, *Phys. Rev. Lett.* **92**, 176803 (2004).

<sup>6</sup> M. Brandbyge, *Nature Nanotechnology* **4**, 81 (2009).

<sup>7</sup> D. Dundas, E. J. McEniry, and T. N. Todorov, *Nature Nanotechnology* **4**, 99 (2009).

<sup>8</sup> Y. C. Chen, *Phys. Rev. B* **78**, 233310 (2008).

<sup>9</sup> M. Galperin, M. A. Ratner, and A. Nitzan, *J. Phys.: Condens. Matter* **19**, 103201 (2007).

<sup>10</sup> Y. C. Chen, M. Zwolak and M. Di Ventra, *Nano Lett.* **3**, 1691 (2003); *Nano Lett.* **4**, 1709 (2004); *Nano Lett.* **5**, 813 (2005).

<sup>11</sup> Z. Huang, B. Xu, Y. C. Chen, M. Di Ventra, and N. J. Tao, *Nano Lett.* **6**, 1240 (2006).

<sup>12</sup> J. G. Kushmerick, J. Lazorcik, C. H. Patterson, and R. Shashidhar, *Nano Lett.* **4**, 639 (2004).

<sup>13</sup> N. Sergueev, D. Roubtsov, and H. Guo, *Phys. Rev. Lett.* **95**, 146803 (2005).

<sup>14</sup> L. H. Yu, C. D. Zangmeister, and J. G. Kushmerick, *Phys. Rev. Lett.* **98**, 206803 (2007).

<sup>15</sup> M. Tsutsui, M. Taniguchi, and T. Kawai, *Nature Commun.* **1**, 138 (2010).

<sup>16</sup> B. C. Hsu, Y.-S. Liu, S. H. Lin, and Y. C. Chen, *Phys. Rev. B* **83**, 041404(R) (2011).

<sup>17</sup> M. Kiguchi, O. Tal, S. Wohlthat, F. Pauly, M. Krieger, D. Djukic, J. C. Cuevas, and J. M. van Ruitenbeek, *Phys. Rev. Lett.* **101**, 046801 (2008).

<sup>18</sup> N. D. Lang, *Phys. Rev. B* **52**, 5335 (1995); M. Di Ventra and N. D. Lang, *Phys. Rev. B* **65**, 045402 (2001).

<sup>19</sup> M. Di Ventra, S. T. Pantelides, and N. D. Lang, *Phys. Rev. Lett.* **88**, 046801 (2002).

<sup>20</sup> M. Di Ventra, S. T. Pantelides, and N. D. Lang, *Phys. Rev. Lett.* **84**, 979 (2000).

<sup>21</sup> K. R. Patton and M. R. Geller, *Phys. Rev. B* **64**, 155320 (2001).